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DEVELOPMENT OF COMPOSITIONS FOR REFRACTORY MATERIAL CONTAINING ALUMINOMAGNESIAN SPINEL

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The dehydration of a hydrated mixture of alumina cement and a magnesial binder produces a heat-resistant material based on aluminomagnesian spinel with a uniform crystallization, It is established that the use of the method proposed makes it possible not only to regulate the composition of the heat-resistant material but also to significantly lower the temperature of the synthesis of minerals.

Intensification of thermal processes and efficient performance of thermal machinery in various sectors of industry is related to applying materials capable of withstanding the joint effect of several factors, such as high temperatures, thermal shocks, aggressive media, etc. At present specially produced articles and lining mixtures are used as refractory lining.

The efficiency of heat-resistant concretes is determined by the properties of the binder and the filler. A heat-resistant concrete and a solution used as lining in thermal machines should have an increased strength growth rate, high refractoriness, preservation of sufficient strength in heating, when hydrates are transformed into anhydrous compounds, as well as resistance in aggressive media.

Analysis of published data shows that heat-resistant properties can be improved by introducing more refractory additives into a clinker mixture in firing or into a cement in milling (or in concrete preparation) [1, 2].

The purpose of our study is the production of aluminomagnesian spinel and a binder with preset properties containing aluminomagnesian spinel.

The raw materials used to obtain aluminomagnesian spinel and cement on its basis were α-Al_2O_3 and MgO with the contents of the main compounds over 98.50 and over 97.18%,[2] respectively.

To accomplish the purpose mentioned above, cement containing aluminomagnesian spinel was produced. The following mixture was used (%): 60 aluminomagnesian spinel and 40 calcium aluminate $CaO \cdot Al_2O_3$.

To identify the thermal transformations occurring in firing of the mixture, differential-thermal analysis was performed with a preset ratio of the initial oxides. It was found that the formation of spinel occurs within the temperature interval of 1280 – 1460°C. The synthesis of calcium aluminates starts at a temperature of 860°C.

To identify the phase composition and the firing kinetics, x-ray phase analysis of mixtures in the systems $MgO – Al_2O_3$ and $CaO – MgO – Al_2O_3$ was carried out. It was found that the formation of spinel in the system $MgO – Al_2O_3$ starts at a temperature of 800°C.

As the temperature and firing duration increase, the intensity of the analytical lines of aluminomagnesian spinel grows (interplanar distances of 0.4680, 0.2863, 0.2442, 0.2386, 0.2025, 0.1653, 0.1558, 0.1431, and 0.1376 nm). However, the synthesis is not complete, since the characteristic peaks of the initial oxides are registered, although their intensity decreases significantly.

The petrography study indicated that the cements produced by firing at 1200°C contain a substantial amount of free Al_2O_3.

An increase in the firing temperature leads to the crystallization of stable rhombic calcium aluminate $CaO \cdot Al_2O_3$ in the form of short-prismatic crystals located on the periphery of Al_2O_3 grains. The amount of calcium aluminates increases, whereas the quantity of initial Al_2O_3 decreases. The formation of an isotropic vitreous phase is registered in the form of melted sites ranging from 15 to 25 μm. The quantity of the emerging melt is 3 vol.%. Grains of Al_2O_3 are visible in this melt. Aluminomagnesian spinel in its pure form is not present; apparently, it is contained in calcium aluminates and forms solid solutions.

Therefore, in the production of aluminomagnesian spinel it is advisable to use intensifying agents that form a melt under firing.

To determine the hydraulic properties of cement based on aluminomagnesian spinel, the materials after firing were milled to a specific surface area of 300 – 350 m^2/kg. The

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[2] Here and elsewhere mass content unless otherwise specified.

TABLE 1

Temperature of cement formation, °C	Normal thickness, %	Setting time, min		Bending/compressive strength, MPa, of samples aged, days			
		start	end	1	3	7	28
1200	34.7	6	11	2.1/7.9	2.4/9.5	1.8/7.5	0.9/2.1
1400	30.7	55	90	8.8/34.4	10.6/52.0	13.7/66.9	15.2/66.9

TABLE 2

Ratio MB : AC	Normal thickness, %	Setting time, min		Bending/compressive strength, MPa, of samples aged, days			
		start	end	1	3	7	28
30 : 70	28.0	13	28	0.03/1.20	8.30/35.00	9.80/53.60	11.00/48.50
50 : 50	28.3	44	89	0.60/8.30	6.00/13.50	5.70/10.50	6.40/16.00
70 : 30	30.0	9	22	1.00/17.70	5.20/19.00	6.70/21.10	8.00/23.70

physicomechanical characteristics of the cements are given in Table 1.

It is established that cement based on aluminomagnesian spinel produced at temperatures of 1200 – 1400°C actively reacts with water, which is due to the presence of calcium monoaluminate in its composition. With increasing firing temperature the normal thickness decreases and the setting period grows. This is due to the fact that the presence of oxide calcium that has not entered into the reaction of calcium aluminate formation has a perceptible effect on the normal thickness and the setting time.

To determine the strength parameters of cements, samples of size 1 × 1 × 3 cm were prepared. The tests were performed on the 1st, 3rd, 7th and 28th day of hardening in the air-moist conditions (Table 1). As the hardening period of the cement produced at 1200°C increases, a decrease in its strength is registered, whereas the cement produced at 1400°C has high strength values in the early, as well as in the final hardening period, which is related to the formation of calcium aluminate in firing. At the temperature of 1200°C the processes of formation of calcium aluminate minerals are incomplete. The great quantity of CaO that has not reacted determines the low strength parameters. Therefore, the optimum firing temperature at which the mineral formation processes are the most complete is 1400°C.

Consequently, the synthesized cement has high hydration activity and high strength both in the early and in the final hardening stages, which is due to the fact that apart from aluminomagnesian spinel that has no binding properties calcium aluminates are formed as well.

At the next stage of our research we produced an aluminomagnesian material at a decreased temperature by dehydration of hydrated alumina cement (AC) and magnesian binder (MB). The alumina cement had the following chemical composition (%): 6.40 SiO_2, 38.0 Al_2O_3, 12.20 Fe_2O_3, 37.50 CaO, 0.32 MgO, and 5.58 other. The mineralogical composition of the cement is (%): 42.0 $CaO \cdot Al_2O_3$, 48,0 $2CaO \cdot Al_2O_3$, and 10.0 other. The composition of caustic magnesite is (%): 80.0 MgO, 2.5 CaO, 2.0 SiO_2, and 2.8 R_2O_3. The calcination loss is 8%, the loss after hydration is 25%; the degree of hydration is 93%, which corresponds to the grade PMKMk-80 (GOST 1216–87).

Different mixtures of MB and AC molded with different water : solid ratios and using the plasticizer S-3 were used. The physicomechanical properties of the mixtures are listed in Tables 2 and 3. It can be seen that the optimum are the mixtures with MB : AC ratios equal to 70 : 30 and 30 : 70.

Hydrated mixtures were later subjected to thermal treatment at various temperatures (Fig. 1).

Analysis of experimental data indicated that the process of $CaO \cdot Al_2O_3$ formation in the temperature interval of 1100 – 1400°C is satisfactorily described by the Tamman – Fishback equation. The reaction rate constant varies within narrow limits (2%). The reaction rate constant found from other equations varies within the limits of 40 – 76%.

It follows from the above data that the main products of hydration of the mixture of MB and AC are calcium hydroaluminates $CaO \cdot Al_2O_3 \cdot 10H_2O$, $2CaO \cdot Al_2O_3 \cdot 8H_2O$, and $4CaO \cdot Al_2O_3 \cdot (13 – 19)H_2O$, as well as $Mg(OH)_2$ in the form of brucite and aluminum hydroxide in the form of boehmite and bayerite, which is corroborated by petrography and electron-microscope analysis (Fig. 2*a*).

TABLE 3

Ratio MB : AC	Bending/compressive strength, MPa, of samples aged for, days			
	1	3	7	28
30 : 70	0.10/1.20	4.50/12.60	6.90/16.60	5.30/18.50
50 : 50	0.20/2.00	0.70/2.30	1.20/13.00	3.00/9.90
70 : 30	0.50/14.30	4.80/12.90	6.60/16.90	4.90/16.20
30 : 70*	0.98/3.10	4.50/10.40	6.00/13.90	5.10/14.00
70 : 30*	2.80/11.50	2.90/10.30	4.10/14.70	6.45/15.90

* 0.5% plasticizer S-3 added.

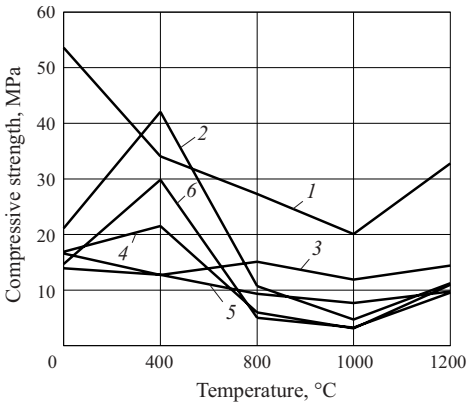

Fig. 1. Strength characteristics of samples heat-treated at different temperatures: *1*, *2*) mixtures containing 30 and 70% MB formed under normal thickness; *3*, *4*) the same formed at a water : solid ratio of 0.4; *5*, *6*) the same formed at a water : solid ratio equal to 0.4 containing 0.5% plasticizer S-3.

After heat treatment at a temperature of 400°C oval-fibrous interlayers of a complex ion-adsorbed compound containing calcium and aluminum ions $CaO \cdot Al_2O \cdot 10H_2O$ between hydrated MgO and Al_2O_3 are formed on the surface of hydrated MgO.

A further increase in the heat treatment temperature up to 1200°C leads to the formation of a strong skeleton consisting of $CaO \cdot Al_2O_3$ crystals of the prismatic-fibrous shape. In this agglomeration grains of $12CaO \cdot 7Al_2O_3$ and $CaO \cdot 2Al_2O_3$ are nonuniformly cemented. The rest is represented by aluminum-magnesian spinel (Fig. 2*b*).

Thus, dehydration of a hydrated mixture of alumina cement and the magnesian binder produces a refractory material based on aluminomagnesia spinel with uniform crystallization. The dehydration of hydrated mixtures makes it possible not only to control the composition of the heat-resistant material but also to significantly lower the temperature of the synthesis of minerals, which makes it possible to control heat-resistant properties in cement and concrete based on this cement.

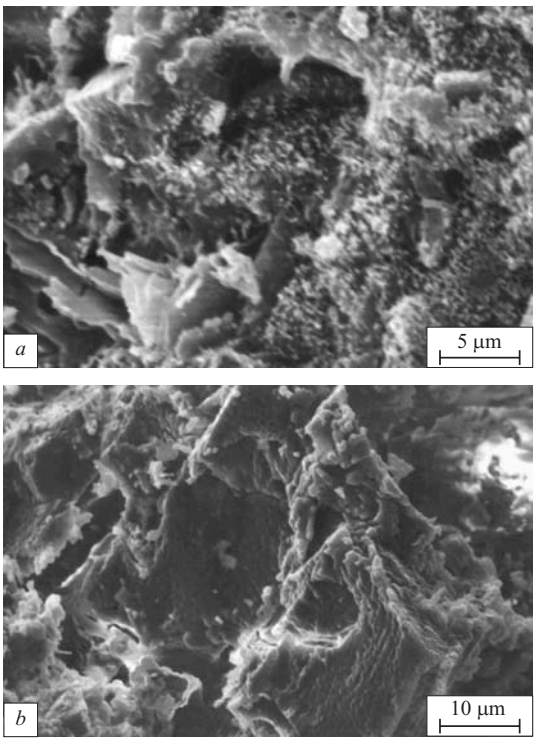

Fig. 2. Electron microscope photos of hydrated samples of mixture MB : AC = 30 : 70 mixed under normal thickness and cured for 7 days (*a*) and also of samples fired at 1200°C (*b*).

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